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**EUROPEAN PATENT APPLICATION**

21 Application number: 84303805.0

51 Int. Cl.<sup>3</sup>: **C 08 F 10/00**  
**C 08 F 4/62**

22 Date of filing: 05.06.84

30 Priority: 06.06.83 US 501688

43 Date of publication of application:  
27.12.84 Bulletin 84/52

84 Designated Contracting States:  
BE DE FR GB IT NL SE

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64 Process and catalyst for polyolefin density and molecular weight control.

67 Catalysts comprising (a) derivatives of mono, bi and tricyclopentadienyl coordination complexes with a transition metal and (b) and an alumoxane are employed in a process of producing polyolefins of controlled molecular weight.

EP 0 129 368 A1

1                   PROCESS AND CATALYST FOR POLYOLEFIN  
2                   DENSITY AND MOLECULAR WEIGHT CONTROL

3           This invention relates to an improved process for  
4           polymerizing olefins and more particularly to a method of  
5           controlling the molecular weight and/or the density of  
6           polyolefins produced so as to obtain polymer product in any  
7           desired range of molecular weight and densities. The invention  
8           particularly relates to the polymerization of the ethylene in  
9           the presence or absence of comonomers to polyethylenes of  
10          controlled molecular weight and density. The invention further  
11          relates to catalyst components and catalyst systems which are  
12          employed for the production of polyolefins of controlled  
13          molecular weight.

14                   DESCRIPTION OF THE PRIOR ART

15          In U. S. Patent 3,051,690 of Vandenberg, issued August 28,  
16          1962, there is described a process of polymerizing olefins to  
17          high molecular weight polyolefins of controlled molecular  
18          weight, as indicated by polymer viscosity, by the addition of  
19          controlled amounts of hydrogen to the polymerization system.  
20          The molecular weight control was described as useful in  
21          combination with a hydrocarbon insoluble catalyst system  
22          comprising the reaction product of a compound of a metal of  
23          Group IVB, VB, VI<sup>B</sup> and VIII with an organometallic compound of  
24          an alkali metal, alkaline earth metal, zinc, earth metal or  
25          rare earth metal. The patent teaches that increased use of  
26          hydrogen during the polymerization process results in the  
27          decrease of polymer product viscosity.

28          It is further known that certain metallocenes such as bis  
29          (cyclopentadienyl) titanium or zirconium dialkyls in  
30          combination with aluminum alkyl/water cocatalyst form  
31          homogeneous catalyst systems for the polymerization of ethylene.

1 German Patent Application 2,608,863 discloses the use of a  
2 catalyst system for the polymerization of ethylene consisting  
3 of bis (cyclopentadienyl) titanium dialkyl, aluminum trialkyl  
4 and water.

5 German Patent Application 2,608,933 discloses an ethylene  
6 polymerization catalyst system consisting of zirconium  
7 metallocenes of the general formula  
8  $(\text{cyclopentadienyl})_n\text{ZrY}_{4-n}$ , wherein n stands for a number in  
9 the range of 1 to 4, Y for R,  $\text{CH}_2\text{AlR}_2$ ,  $\text{CH}_2\text{CH}_2\text{AlR}_2$  and  
10  $\text{CH}_2\text{CH}(\text{AlR}_2)_2$ , wherein R stands for alkyl or metallo  
11 alkyl, an aluminum trialkyl cocatalyst and water.

12 European Patent Appln. No. 0035242 discloses a process for  
13 preparing ethylene and atactic propylene polymers in the  
14 presence of a halogen-free Ziegler catalyst system of (1)  
15 cyclopentadienyl compound of the formula  
16  $(\text{cyclopentadienyl})_n\text{MeY}_{4-n}$  in which n is an interger from 1  
17 to 4, Me is a transition metal, especially zirconium, and Y is  
18 either hydrogen, a  $\text{C}_1\text{-C}_5$  alkyl or metallo alkyl group or a  
19 radical having the following general formula  $\text{CH}_2\text{AlR}_2$ ,  
20  $\text{CH}_2\text{CH}_2\text{AlR}_2$  and  $\text{CH}_2\text{CH}(\text{AlR}_2)_2$  in which R represents a  
21  $\text{C}_1\text{-C}_5$  alkyl or metallo alkyl group, and (2) an alumoxane.

22 The above patents disclose that the polymerization process  
23 employing the homogeneous catalyst system is also hydrogen  
24 sensitive for molecular weight control.

25 An advantage of the cyclopentadienyl-metal/alumoxane  
26 catalyst system, is their extremely high activity for ethylene  
27 polymerization. Another significant advantage is that unlike  
28 olefin polymers produced in the presence of conventional  
29 heterogeneous Ziegler catalyst, terminal unsaturation is  
30 present in polymers produced in the presence of these  
31 homogeneous catalysts. The use of hydrogen for molecular  
32 weight control for these homogeneous catalysts would be  
33 disadvantageous since the terminal unsaturation would become  
34 saturated and hence, the loss of available sites for building  
35 functionalities into the olefin polymers.

As is generally known in the art, it is desirable to maximize polymerization temperatures in order to achieve high polymerization activity and reduce operating costs in terms of energy recovery. The catalyst disclosed in EP 35242 has certain disadvantages for the production of high molecular weight, high density resins since to produce such polymer products, one must operate at low temperatures thereby increasing operating costs and decreasing catalytic activity.

It would be highly desirable to provide homogeneous catalysts which can be usefully employed to produce high molecular weight polymer products at conventional polymerization temperatures and to be able to control molecular weight and density of the polymer product without resorting to temperature control or hydrogen.

## SUMMARY OF THE INVENTION

Accordingly, the present invention provides new cyclopentadienyl-metal/alumoxane catalysts for olefin polymerization which catalyst can be usefully employed at high temperatures to obtain olefin polymer products having excellent properties with respect to molecular weight, density and terminal unsaturation.

It has been discovered that the molecular weight of polymer product can be controlled by the judicious selection of substituent on the cyclopentadienyl ring and use of ligands for the metallocenes. It has further been discovered that comonomer content can be controlled by the judicious selection of metallocenes. Hence, by the selection of catalyst components one can tailor polymer product with respect to molecular weight and density.

1       The catalysts usefully employed for the polymerization of  
 2 ethylene and alpha-olefins to polyethylene homopolyolefins and  
 3 copolyethylene- alpha-olefin comprise new metallocenes in  
 4 combination with alumoxanes. The metallocenes employed in  
 5 accordance with this invention are organometallic coordination  
 6 compounds which are cyclopentadienyl derivatives of a Group 4b,  
 7 5b and 6b metal of the Periodic Table and include mono, di and  
 8 tricyclopentadienyl and their derivatives of the transition  
 9 metals. The metallocenes include those represented by the  
 10 general formula  $(C_5R'_m)_p R''_s (C_5R'_m)MeQ_{3-p}$  or  
 11  $R''_s (C_5R'_m)MeQ'$  wherein Me is a Group 4b, 5b, or 6b metal  
 12 of the Periodic Table (Chemical Rubber Company's Handbook of  
 13 Chemistry & Physics, 48th edition),  $(C_5R'_m)$  is a  
 14 cyclopentadienyl or substituted cyclopentadienyl, each  $R'$ ,  
 15 which can be the same or different, is hydrogen or a  
 16 hydrocarbyl radical such as alkyl, alkenyl, aryl, alkylaryl, or  
 17 arylalkyl radical having from 1 to 20 carbon atoms or two  
 18 carbon atoms are joined together to form a  $C_4-C_6$  ring,  $R''$   
 19 is a  $C_1-C_4$  alkylene radical, a dialkyl germanium or  
 20 silicone, or a alkyl phosphine or amine radical bridging two  
 21  $(C_5R'_m)$  rings, Q is a hydrocarbon radical such as aryl,  
 22 alkyl, alkenyl, alkylaryl, or arylalkyl radical having from 1  
 23 to 20 carbon atoms or halogen and can be the same or different,  
 24 Q' is an alkylidene radical having from 1 to 20 carbon  
 25 atoms, s is 0 or 1, p is 0, 1 or 2; when p is 0, s is 0, m is 4  
 26 when s is 1 and m is 5 when s is 0 and at least one  $R'$  is a  
 27 hydrocarbyl radical when Q is an alkyl radical.

28       The molecular weight of the polymer product can be further  
 29 controlled by the ratio of alumoxane to metallocene.

30       The present invention also provides a process for producing  
 31 polyethylenes having a high molecular weight at relatively high  
 32 temperatures. The process comprises polymerizing ethylene  
 33 alone or in the presence of minor amounts of higher  
 34 alpha-olefins or diolefins in the presence of the catalyst  
 35 system described above.

36       The advantages of this invention are obtained by the use of  
 37 derivatives of the cyclopentadienyl ring and/or other ligands

1 for the metallocenes in order to control and tailor polymer  
2 molecular weight and/or comonomer content.

3 DETAILED DESCRIPTION OF THE INVENTION

4 The present invention is directed towards catalyst systems  
5 and a catalytic process for the polymerization of olefins, and  
6 particularly ethylene to high molecular weight polyethylenes  
7 such as linear low density polyethylene (LLDPE) and high  
8 density polyethylene (HDPE). The polymers are intended for  
9 fabrication into articles by extrusion, injection molding,  
10 thermoforming, rotational molding, and the like. In  
11 particular, the polymers of this invention are homopolymers of  
12 ethylene, and copolymers of ethylene with higher alpha-olefins  
13 having from 3 to 10 carbon atoms and preferably 4 to 8  
14 carbon atoms. Illustrative of the higher alpha-olefins are  
15 butene-1, hexene-1 and octene-1.

16 In the process of the present invention, ethylene, either  
17 alone or together with alpha-olefins having 3 or more carbon  
18 atoms, is polymerized in the presence of a catalyst system  
19 comprising at least one metallocene and an alumoxane.

20 In accordance with this invention, one can also produce  
21 olefin copolymers particularly copolymers of ethylene and  
22 higher alpha-olefins having from 3-18 carbon atoms. As  
23 indicated above, the comonomer content can be controlled  
24 through the selection of metallocene catalyst component.

25 The alumoxanes are polymeric aluminum compounds which can  
26 be represented by the general formulae  $(R-Al-O)_n$  which is a  
27 cyclic compound and  $R(R-Al-O)_nAlR_2$ , which is a linear  
28 compound. In the general formula R is a  $C_1-C_5$  alkyl group  
29 such as, for example, methyl, ethyl, propyl, butyl and pentyl  
30 and n is an integer from 1 to 20. Most preferably, R is  
31 methyl and n is 4. Generally, in the preparation of  
32 alumoxanes from, for example, aluminum trimethyl and water, a  
33 mixture of the linear and cyclic compounds is obtained.

34 The alumoxane can be prepared in various ways. Preferably,  
35 they are prepared by contacting water with a solution of

1 aluminum trialkyl, such as, for example, aluminum trimethyl, in  
 2 a suitable organic solvent such as benzene or an aliphatic  
 3 hydrocarbon. For example, the aluminum alkyl is treated with  
 4 water in the form of a moist solvent. In an alternative  
 5 method, the aluminum alkyl such as aluminum trimethyl can be  
 6 desirably contacted with a hydrated salt such as hydrated  
 7 copper sulfate.

8 Preferably, the alumoxane is prepared in the presence of a  
 9 hydrated copper sulfate. The method comprises treating a  
 10 dilute solution of aluminum trimethyl in, for example, toluene,  
 11 with copper sulfate represented by the general formula  
 12  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . The ratio of copper sulfate to aluminum  
 13 trimethyl is desirably about 1 mole of copper sulfate for 4 to  
 14 5 moles of aluminum trimethyl. The reaction is evidenced by  
 15 the evolution of methane.

16 The new metallocene compounds usefully employed in  
 17 accordance with this invention are the mono, bi and  
 18 tricyclopentadienyl or substituted cyclopentadienyl metal  
 19 compounds. The metallocenes are represented by the general  
 20 formula  $(\text{C}_5\text{R}'_m)_p \text{R}''_s (\text{C}_5\text{R}'_m) \text{MeQ}_{3-p}$  and  
 21  $\text{R}''_s (\text{C}_5\text{R}'_m)_2 \text{MeQ}'$  wherein  $(\text{C}_5\text{R}'_m)$  is a  
 22 cyclopentadienyl or substituted cyclopentadienyl, each  $\text{R}'$  is  
 23 the same or different and is hydrogen or a hydrocarbyl radical  
 24 such as alkyl, alkenyl, aryl, alkylaryl, or arylalkyl radicals  
 25 containing from 1 to 20 carbon atoms or two carbon  
 26 atoms are joined together to form a  $\text{C}_4$ - $\text{C}_6$  ring,  $\text{R}''$  is a  
 27  $\text{C}_1$ - $\text{C}_4$  alkylene radical, a dialkyl germanium or silicone, or  
 28 a alkyl phosphine or amine radical bridging two  $(\text{C}_5\text{R}'_m)$   
 29 rings, Q is a hydrocarbyl radical such as aryl, alkyl, alkenyl,  
 30 alkylaryl, or arylalkyl radical having from 1-20 carbon atoms  
 31 or halogen and can be the same or different,  $\text{Q}'$  is an  
 32 alkylidene radical having from 1 to 20 carbon atoms, s is  
 33 0 or 1, p is 0, 1 or 2; when p is 0, s is 0; m is 4 when s is 1  
 34 and m is 5 when s is 0, at least one  $\text{R}'$  is a hydrocarbyl  
 35 radical when Q is an alkyl radical and Me is a Group 4b, 5b, or  
 36 6b metal.

Exemplary hydrocarbyl radicals are methyl, ethyl, propyl, butyl, amyl, isoamyl, hexo, isobutyl, heptyl, octyl, nonyl, dicyl, cetyl, 2-ethylhexyl, phenyl, and the like.

Exemplary alkylene radicals are methylene, ethylene, propylene, and the like.

Exemplary halogen atoms include chlorine, bromine and iodine and of these halogen atoms, chlorine is preferred.

Exemplary of the alkylidene radicals is methylenidene, ethylenidene and propylenidene.

Of the metallocenes, zirconocenes and titanocenes are most preferred. Illustrative but non-limiting examples of these metallocenes which can be usefully employed in accordance with this invention are monocyclopentadienyls titanocenes such as, cyclopentadienyl titanium trichloride,

pentamethylcyclopentadienyl titanium trichloride;

bis(cyclopentadienyl) titanium diphenyl, the carbene

represented by the formula  $\text{Cp}_2\text{Ti}=\text{CH}_2 \cdot \text{Al}(\text{CH}_3)_2\text{Cl}$

and derivatives of this reagent such as

$\text{Cp}_2\text{Ti}=\text{CH}_2 \cdot \text{Al}(\text{CH}_3)_3$ ,  $(\text{Cp}_2\text{TiCH}_2)_2$ ,

$\text{Cp}_2\text{TiCH}_2\text{CH}(\text{CH}_3)\text{CH}_2$ ,  $\text{Cp}_2\text{Ti}=\text{CHCH}_2\text{CH}_2$ ,  $\text{Cp}_2\text{Ti}=\text{CH}_2$

$\cdot \text{AlR}'''_2\text{Cl}$ , wherein Cp is a cyclopentadienyl or

substituted cyclopentadienyl radical, and R''' is an alkyl, aryl or alkylaryl radical having from 1-18 carbon atoms; substituted

bis(Cp)Ti(IV) compounds such as

bis(indenyl)Ti diphenyl or dichloride,

bis(methylcyclopentadienyl)Ti diphenyl or dihalides and other

dihalide complexes; dialkyl, trialkyl, tetra-alkyl and

penta-alkyl cyclopentadienyl titanium compounds such as

bis(1,2-dimethylcyclopentadienyl)Ti diphenyl or dichloride,

bis(1,2-diethylcyclopentadienyl)Ti diphenyl or dichloride and

other dihalide complexes; silicone, phosphine, amine or carbon

bridged cyclopentadiene complexes, such as dimethyl

silyldicyclopentadienyl titanium diphenyl or dichloride, methyl

phosphine dicyclopentadienyl titanium diphenyl or dichloride, methyl-

enedicyclopentadienyl titanium diphenyl or dichloride, ethylene bis

(4, 5, 6, 7-tetrahydroindenyl)titanium dichloride and other dihalide

complexes and the like.



1 Illustrative but non-limiting examples of the zirconocenes  
2 which can be usefully employed in accordance with this  
3 invention are, cyclopentadienyl zirconium trichloride,  
4 pentamethylcyclopentadienyl zirconium trichloride,  
5 bis(cyclopentadienyl)zirconium diphenyl,  
6 bis(cyclopentadienyl)zirconium dimethyl, the alkyl substituted  
7 cyclopentadienes, such as bis(ethyl cyclopentadienyl)zirconium  
8 dimethyl, bis(8-phenylpropylcyclopentadienyl)zirconium  
9 dimethyl, bis(methylcyclopentadienyl)zirconium dimethyl, and di-  
10 halide complexes of the above; di-alkyl, tri-alkyl, tetra-alkyl, and  
11 penta-alkyl cyclopentadienes, such as bis(tetramethylcyclopentadie-  
12 nyl)zirconium dimethyl, bis(pentamethylcyclopentadienyl)zirconium  
13 dimethyl, bis(1,2-dimethylcyclopentadienyl)zirconium dimethyl,  
14 bis(1,3-diethylcyclopentadienyl)zirconium dimethyl and dihalide  
15 complexes of the above; silicone, phosphorus, and carbon  
16 bridged cyclopentadiene complexes such as  
17 dimethylsilyldicyclopentadienyl zirconium dimethyl or dihalide,  
18 methylphosphine dicyclopentadienyl zirconium dimethyl or  
19 dihalide, and methylene dicyclopentadienyl zirconium dimethyl  
20 or dihalide, carbenes represented by the formulae  
21  $\text{Cp}_2\text{Zr}=\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2\text{CH}_3$ , and derivatives of these  
22 compounds such as  $\text{Cp}_2\text{ZrCH}_2\text{CH}(\text{CH}_3)\text{CH}_2$ .

23 Bis(cyclopentadienyl)hafnium dichloride,  
24 bis(cyclopentadienyl)hafnium dimethyl,  
25 bis(cyclopentadienyl)vanadium dichloride and the like are  
26 illustrative of other metallocenes.

27 The ratio of aluminum in the alumoxane to total metal in  
28 the metallocenes can be in the range of 0.5:1 to  
29 10,000:1, and preferably 5:1 to 1000:1.

30 The solvents used in the preparation of the catalyst system  
31 are inert hydrocarbons, in particular a hydrocarbon that is  
32 inert with respect to the catalyst system. Such solvents are  
33 well known and include, for example, isobutane, butane,  
34 pentane, hexane, heptane, octane, cyclohexane,  
35 methylcyclohexane, toluene, xylene and the like.

36 As a further control and refinement of polymer molecular  
37 weight, one can vary the concentration alumoxane. Higher

1 concentrations of alumoxane in the catalyst system results in  
2 higher polymer product molecular weight.

3 Since, in accordance with this invention, one can produce  
4 high viscosity polymer product at relatively high temperature,  
5 temperature does not constitute a limiting parameter as with  
6 the prior art metallocene/alumoxane catalyst. The catalyst  
7 systems described herein, therefore, are suitable for the  
8 polymerization of olefins in solution, slurry or gas phase  
9 polymerizations and over a wide range of temperatures and  
10 pressures. For example, such temperatures may be in the range  
11 of  $-60^{\circ}\text{C}$  to  $280^{\circ}\text{C}$  and especially in the range  
12 of  $50^{\circ}\text{C}$  to  $160^{\circ}\text{C}$ . The pressures employed in  
13 the process of the present invention are those well known for,  
14 for example, in the range of about 1 to about 500 atmospheres  
15 and greater.

16 In a solution phase polymerization the alumoxane is  
17 preferably dissolved in a suitable solvent, typically in inert  
18 hydrocarbon solvent such as toluene, xylene, and the like in  
19 molar ratios of about  $5 \times 10^{-3}$ M. However greater or lesser  
20 amounts can be used.

21 The soluble metallocenes can be converted to supported  
22 heterogeneous catalyst by depositing said metallocenes on  
23 typical catalyst supports such as, for example, silica,  
24 alumina, and polyethylene. The solid catalysts in combination  
25 with an alumoxane can be usefully employed in slurry and gas  
26 phase olefin polymerizations.

27 After polymerization and deactivation of the catalyst, the  
28 product polymer can be recovered by processes well known in the  
29 art for removal of deactivated catalysts and solution. The  
30 solvents may be flashed off from the polymer solution and the  
31 polymer obtained extruded into water and cut into pellets or  
32 other suitable comminuted shapes. Pigments, antioxidants and  
33 other additives, as is known in the art, may be added to the  
34 polymer.

35 The polymer product obtained in accordance with this  
36 invention will have a weight average molecular weight in the  
37 range of 1,400,000 to 500 and preferably 500,000 to

1           1000.

2           The polydispersities (molecular weight distribution)  
3           expressed as  $\bar{M}_w/\bar{M}_n$  are typically from 1.5 to 4.0. The polymers  
4           contain 1.0 chain end insaturation per molecule. Broadened MW  
5           can be obtained by employing two or more of the metal  
6           cyclopentadienyls in combination with the alumoxane as  
7           described in cofiled application entitled Process and Catalyst  
8           for Producing Polyethylene having a Broad Molecular Weight  
9           Distribution.

10          The polymers produced by the process of this present  
11          invention are capable of being fabricated into a wide variety  
12          of articles, as is known for homopolymers of ethylene and  
13          copolymers of ethylene and higher alpha-olefins. The present  
14          invention is illustrated by the following examples.

15          EXAMPLES

16          In the examples following the molecular weights were  
17          determined on a Water's Associates Model No. 150C GPC (Gel  
18          Permeation Chromatography). The measurements were made by  
19          dissolving polymer samples in hot trichlorobenzene (TCB) and  
20          filtered. The GPC runs were performed at 145°C in TCB at 1.5  
21          ml/min using two Shodex A80 M/S Gel columns of 9.4 mm internal  
22          diameter from Perkin Elmer Inc. 300 milliliter of 3.1 percent  
23          solutions in TCB were injected and the chromatographic runs  
24          monitored at sensitivity equal -64 and scale factor equal 65.  
25          The samples were run in duplicate. The integration parameters  
26          were obtained with a Water's Associates data module. An  
27          antioxidant, N-phenyl-2-naphthylamine, was added to all samples.

28          In the examples following the alumoxane was prepared in the  
29          following manner:

30          600cc of a 14.5% solution of triamethylaluminum (TMA) in  
31          heptane was added in 30cc increments at 5 minute intervals,  
32          with rapid stirring, to 200cc toluene in a Zipperclave reactor  
33          under nitrogen and maintained at 100°C. Each increment was  
34          immediately followed by the addition of 0.3cc water. The  
35          reactor was vented of methane after each addition. Upon  
36          completion of the addition, the reactor was stirred for 6 hours

1 while maintaining the temperature at 100°C. The mixture,  
2 containing soluble alumoxane and a small quantity of insoluble  
3 alumina, is allowed to cool to room temperature and settle.  
4 The clear solution containing the soluble alumoxane is  
5 separated by decontation from the solids.

6 The molecular weights were determined by gel permeation  
7 chromatography at 145°C on a Waters GPC 150C.

8 Example 1

9 A 1-liter stainless steel pressure vessel, equipped with an  
10 incline blade stirrer, an external water jacket for temperature  
11 control, a septum inlet and vent line, and a regulated supply  
12 of dry ethylene and nitrogen, was dried and decxygenated with a  
13 nitrogen flow. 500cc of dry, degassed toluene was introduced  
14 directly into the pressure vessel. 10.0cc of 0.785 molar (in  
15 total aluminum) alumoxane was injected into the vessel by a gas  
16 tight syringe through the septum inlet and the mixture was  
17 stirred at 1,200 rpms and 80°C for 5 minutes at 0 psig of  
18 nitrogen. 0.091 mg bis(cyclopentadienyl) zirconium dichloride  
19 dissolved in 2.0 ml of dry, distilled toluene was injected  
20 through the septum inlet into the vessel. After 1 minute,  
21 ethylene at 60 psig was admitted and while the reaction vessel  
22 was maintained at 80°C. The ethylene was passed into the  
23 vessel for 30 minutes at which time the reaction was stopped by  
24 rapidly venting and cooling. 13.6 gms of powdery white  
25 polyethylene having a  $\bar{M}_n$  of 39,500 and a  $\bar{M}_w$  of 140,000 with a  
26 molecular weight distribution of 3.5.

27 Example 2

28 A 1-liter stainless steel pressure vessel, equipped with an  
29 incline blade stirrer, an external water jacket for temperature  
30 control, a septum inlet and vent line, and a regulated supply  
31 of dry ethylene and nitrogen, was dried and deoxygenated with a  
32 nitrogen flow. 400cc of dry, degassed toluene was introduced  
33 directly into the pressure vessel. 20.0cc of alumoxane  
34 (.785mmoles in total aluminum) was injected into the vessel by  
35 a gas tight syringe through the septum inlet and the mixture

1 was stirred at 1,200 rpms and 80°C for 5 minutes at 0 psig of  
2 nitrogen. 0.2101 mg bis(methylcyclopentadienyl) zirconium  
3 dichloride dissolved in 2.0 ml of dry, distilled toluene was  
4 injected through the septum inlet into the vessel to give an  
5 Al/Zr ratio of  $24 \times 10^3$ . After 1 minute, ethylene at 60 psig  
6 was admitted for 30 minutes while maintaining the reaction  
7 vessel at 80°C. The reaction was stopped by rapidly venting  
8 and cooling. 28.6 gms of powdery white polyethylene having a  
9  $\bar{M}_n$  of 55,900 and a  $\bar{M}_w$  of 212,000 with a molecular weight  
10 distribution of 3.8 and activity (Kg/gM.hr.atm) of 467.

11 Example 3 - 6

12 Examples 3-6 were performed as Example 2 except that the  
13 metallocenes listed in Table 1 were substituted for the  
14 metallocene in Example 2. The results of the examples are  
15 summarized in Table I.

16 Examples 7 - 9

17 Examples 7-9 were performed as Example 2 except that 0.2 mg  
18 of metallocenes as listed in Table 2 and 9.0 cc alumoxane were  
19 employed giving an Al/Zr of  $8 \times 10^3$ . The results are  
20 summarized in Table 2.

TABLE I - Substituted Cyclopentadiene (Cp) Ligand Effects

<u>Example</u>	<u>Catalyst<sup>a</sup></u>	<u><math>\bar{M}_w</math></u>	<u><math>\bar{M}_n</math></u>	<u>MWD</u>	<u>Activity Kg/gM.hr.atm</u>
2	$\text{Cp}_2\text{ZrCl}_2$	140,000	39,500	3.5	252
3	$(\text{MeCp})_2\text{ZrCl}_2$	212,000	55,900	3.8	467
4	$(\text{EtCp})_2\text{ZrCl}_2$	171,000	44,700	3.8	306
5	$(\text{B-PP-Cp})_2\text{ZrCl}_2$ <sup>b</sup>	282,000	78,200	3.6	335
6	$(\text{Me}_5\text{Cp})_2\text{ZrCl}_2$	63,000	13,200	4.7	71

a. Al/Zr=24,000

b. PP = phenyl propyl

TABLE II

<u>Example</u>	<u>Catalyst<sup>a</sup></u>	<u><math>\bar{M}_w</math></u>	<u><math>\bar{M}_n</math></u>	<u>MWD</u>	<u>Activity Kg/gM.hr.atm</u>
7	$(\text{Me}_5\text{Cp})_2\text{ZrCl}_2$	47,300	13,200	3.6	142
8	$(\text{MeCp})_2\text{ZrCl}_2$	180,000	48,300	3.7	278
9	$(\text{EtCp})_2\text{ZrCl}_2$	184,000	50,000	3.7	281

a. Al/Zr=8,000

1       The physical properties of a polyethylene are largely  
2 determined by the polymer molecular weight and the polymer  
3 density. The previous examples have demonstrated that through  
4 the ligand effect, one can control the molecular weight of  
5 polyethylenes. The following examples demonstrate that through  
6 the same ligand effects, one can control the polymer density in  
7 copolymerse such as ethylene copolymers. In addition, the  
8 control of polymer density in the following examples is  
9 demonstrated at fixed reaction conditions indicating that  
10 density control is mediated by ligand effects on the catalyst  
11 reactivity ratios.

12       Example 10

13       A 1-liter stainless steel pressure vessel, equipped with an  
14 incline blade stirrer, an external water jacket for temperature  
15 control, a septum inlet and vent line, and a regulated supply  
16 of dry ethylene and nitrogen, was dried and deoxygenated with a  
17 nitrogen flow. 400cc of dry, degassed toluene was introduced  
18 directly into the pressure vessel. 10.0cc of alumoxane  
19 solution (0.8 moles in total aluminum) was injected into the  
20 vessel by a gas tight syringe through the septum inlet and the  
21 mixture was stirred at 1,200 rpms and 50°C for 5 minutes at 0  
22 psig of nitrogen. 200cc of liquid propylene at 25°C was then  
23 added resulting in a pressure of 126.2 psig. 0.113 mg of  
24 bis(cyclopentadienyl)zirconium dimethyl in 10 ml of toluene was  
25 injected through the septum inlet into the vessel. Ethylene at  
26 152.1 psig was admitted and the reaction vessel was maintained  
27 at 50°C. The ethylene was passed into the vessel for 30  
28 minutes at which time the reaction was stopped by rapidly  
29 venting and cooling the reactor. 66.0 gms of copolymer having  
30 an intrinsic viscosity of 0.74 was isolated which contained 31  
31 mole % propylene. The density was 0.854 g/cc at 23°C.

1     Example 11

2         A 1-liter stainless steel pressure vessel, equipped with an  
3     incline blade stirrer, an external water jacket for temperature  
4     control, a septum inlet and vent line, and a regulated supply  
5     of dry ethylene and nitrogen, was dried and deoxygenated with a  
6     nitrogen flow. 400cc of dry, degassed toluene was introduced  
7     directly into the pressure vessel. 10.0cc of alumoxane  
8     solution (0.8 moles in total aluminum) was injected into the  
9     vessel by a gas tight syringe through the septum inlet and the  
10    mixture was stirred at 1,200 rpms and 50°C for 5 minutes at 0  
11    psig of nitrogen. 200cc of liquid propylene at 25°C was then  
12    added resulting in a pressure of 126.2 psig. 0.102 mg of  
13    dimethylsilyl-cyclopentadienyl zirconium chloride in 10 ml of  
14    toluene was injected through the septum inlet into the vessel.  
15    Ethylene at 152.4 psig was admitted and the reaction vessel was  
16    maintained at 50°C. The ethylene was passed into the vessel  
17    for 30 minutes at which time the reaction was stopped by  
18    rapidly venting and cooling the reactor. 12.0 gms of copolymer  
19    having an intrinsic viscosity of 0.52 was isolated which  
20    contained 43 mole % propylene. The density was 0.854 g/cc at  
21    23°C.

22    Example 12

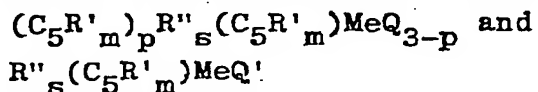
23         A 1-liter stainless steel pressure vessel, equipped with an  
24    incline blade stirrer, an external water jacket for temperature  
25    control, a septum inlet and vent line, and a regulated supply  
26    of dry ethylene and nitrogen, was dried and deoxygenated with a  
27    nitrogen flow. 400cc of dry, degassed toluene was introduced  
28    directly into the pressure vessel. 10.0cc of alumoxane  
29    solution (0.8 moles in total aluminum) was injected into the  
30    vessel by a gas tight syringe through the septum inlet and the  
31    mixture was stirred at 1,200 rpms and 50°C for 5 minutes at 0  
32    psig of nitrogen. 200cc of liquid propylene at 25°C was then



1 added resulting in a pressure of 126.2 psig. 0.417 mg of  
2 bis(pentamethylcyclopentadienyl)zirconium dimethyl in 10 ml of  
3 toluene was injected through the septum inlet into the vessel.  
4 Ethylene at 151.5 psig was admitted and the reaction vessel was  
5 maintained at 50°C. The ethylene was passed into the vessel  
6 for 25 minutes at which time the reaction was stopped by  
7 rapidly venting and cooling the reactor. 30.5 gms of copolymer  
8 having an intrinsic viscosity of 0.81 was isolated which  
9 contained 3.6 mole % propylene. The density was 0.934 g/cc at  
10 23°C.

CLAIMS

1. A metallocene for use as a catalyst component for olefin polymerization, being a compound of the general formula:



wherein Me is a Group 4b, 5b, 6b metal,  $(C_5R'_m)$  is a cyclopentadienyl or substituted cyclopentadienyl, each  $R'$ , which can be the same or different, is hydrogen, an alkyl, alkenyl, aryl, alkylaryl, or arylalkyl radical having from 1 to 20 carbon atoms or two  $R'$  substituents together form a fused  $C_4-C_6$  ring,  $R''$  is a  $C_1-C_4$  alkylene radical, a dialkyl germanium or silicone, or an alkyl phosphine or amine radical bridging two  $(C_5-R'_m)$  rings, each  $Q$ , which can be the same or different, is aryl, alkyl, alkenyl, alkylaryl, or arylalkyl radical having from 1 to 20 carbon atoms or halogen,  $Q'$  is an alkylidene radical having from 1 to 20 carbon atoms,  $s$  is 0 or 1,  $p$  is 0, 1 or 2; when  $p$  is 0,  $s$  is 0;  $m$  is 4 when  $s$  is 1; and  $m$  is 5 when  $s$  is 0 and at least one  $R'$  is a hydrocarbyl radical when  $Q$  is an alkyl radical.

2. The compound of claim 1 wherein  $p$  is 0,  $Q$  is chlorine and  $R'$  is methyl or ethyl.

3. bis(Cyclopentadienyl) titanium diphenyl  
bis(cyclopentadienyl)  $Ti=CH_2Al(CH_3)_2Cl$ ,  
bis(cyclopentadienyl) zirconium dichloride,  
bis(methylcyclopentadienyl) zirconium dichloride,  
bis(ethylcyclopentadienyl) zirconium dichloride,  
bis( $\beta$ -phenylpropylcyclopentadienyl) zirconium dichloride  
bis(pentamethylcyclopentadienyl) zirconium dichloride  
bis(tetramethylcyclopentadienyl) zirconium dimethyl,  
bis(cyclopentadienyl) zirconium dimethyl,  
bis(ethylcyclopentadienyl) zirconium dimethyl, or  
ethylene bis(4, 5, 6, 7-tetrahydroindenyl)titanium dichloride.

4. A catalyst system for the polymerization of olefins comprising a compound of any of claims 1 to 3 and an alumoxane.

5. A process for polymerizing one or more olefins which comprises conducting the polymerization in the presence of a catalyst system as claimed in claim 4.

6. The process of claim 5 wherein the olefin is ethylene or an alpha-olefin having from 3 to 8 carbon atoms.



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# EUROPEAN SEARCH REPORT

0129368

Application number

EP 84 30 3805

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
X	EP-A-0 069 951 (HOECHST) * claims 1-8; examples 2,3,4 *	1,3-6	C 08 F 10/00 C 08 F 4/62
X,D	EP-A-0 035 242 (SINN, HANSJÖRG) * claims 1,2 *	1,3-6	
X	DIE MAKROMOLEKULARE CHEMIE, vol. 182, no. 4, April 16, 1981 HEIDELBERG (DE) J. CIHLÄR et al.: "Polymerization of Ethylene Catalyzed by Titanocene Systems, 2a, Catalytic Systems CP2 TiRCI/Oxyaluminium Compounds", pages 1127-113 4. * page 1133, tabel no. 2 and no. 7 *	1,3-5	
X	US-A-3 161 629 (R.D. GORSICH et al.) * claim 1; column 1, line 63 - column 3, line 17 *	1,2	TECHNICAL FIELDS SEARCHED (Int. Cl. 7)  C 08 F
X	FR-A-2 072 484 (BAYER) * claim 1; page 1, lines 15-34; page 2, lines 19-25; examples 1-3 *	1,2	
X,D	DE-A-2 608 933 (BASF) * claim *	1,3-5	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 13-09-1984	Examiner WEBER H.
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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
X,D	DE-A-2 608 863 (BASF) * claims *  -----	1,3-5	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 7)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 13-09-1984	Examiner WEBER H.
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